PHASE TRANSFER CATALYSED REDUCTION OF NITROACETOPHENON TO AMINOACETOPHENON BY H_2S-RICH AQUEOUS METHYLDIETHANOLAMINE USING TETRABUTYLPHOSPHONIUM BROMIDE

by

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CERTIFICATE

This is to certify that thesis entitled reduction of "**nitroacetophenon to aminoacetophenon by h_2s-rich aqueous methyldiethanolamine a novel process for utilization of h_2s-laden gas streams using tetrabutylphosphonium bromide as phase transfer catalysis"** which is submitted by **Mr. Smruti Ranjan Sethi, Roll No: 111CH0583** in partial fulfilment of the requirement for the award of degree B.Tech. in Chemical Engineering to National Institute of Technology Rourkela is a record of the candidate own work carried out by him in the Department of Chemical Engineering National Institute of Technology under my supervision & guidance.

The thesis submitted by Mr. S.R. Sethi, is worthy of consideration for the partial fulfilment of award of the degree of "Bachelor of Technology" in accordance with the regulations of this Institute. The results incarnated in the report are authentic to the best of my knowledge.

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ABSTRACT

Industrialisation & environmental pollution are two faces of a coin. To reduce the negative impact of pollution chemical research & engineering has accepted green chemistry to minimize use & generation of hazardous substance. This thesis is regarding the economical use of hazardous substance H_2S, generally found in a lot of industrial process with flue gas, by a method involving sustainable chemistry.

Hydrogen sulphide or sulfane is a colourless gas with a fetor & pungent rotten egg odour. H_2S gas is highly toxic, corrosive & flammable in nature. Natural occurrence of hydrogen sulphide is due to volcano, hot springs, sulfate reducing bacteria found in natural cycle of sulphur. A very small amount of hydrogen sulphide occur in crude petroleum but natural gas contains abundant amount of hydrogen sulphide. Mostly in refineries sour gas comes as the by-product. H_2S gas possess quite serious threat to health issue depending on the time exposed to hydrogen sulphide & concentration of the hydrogen sulphide you breathe. It causes slight irritation/ burning of eyes, suffocation & even knockdown.

So refineries have constantly making effort for a better economical green chemistry method to treat sour gas by-product streams in industry. Presently in industry Claus process is the most efficient desulphurization process in recovering elemental sulphur. But elemental sulphur is not a good economical product as its only use is production of sulphuric acid followed by fertilizer & stripping of H_2S from alkanolamine costs a lot. So the idea behind this project is to bargain a substitute for Claus process. The present study involves synthesis of aminoacetophenon using H_2S rich aq. n-methyldiethanolamine in the presence of PTC, tetrabutylphosphonuim bromide & also kinetic study of effect of variations of temperature, stirring speed, catalyst loading, reactant concentration & sulfide concentration. The application of aminoacetophenon are manufacturing of products with commercial importance like synthesis of variety pharmaceutical products, synthesis of new effective catalysts for various process, pesticide, HPCL silica monolith, preparation of unnatural amino alcohol, bee repellents, Immobilization of E. Coli & much more small uses like Spectrophotometric determination of isoproturon etc. from hydrogen sulphide instead of converting into elemental sulphur or disulphide. Thus hydrogen sulphide gas is utilized in a better economical way.

Key words:- desulphurization, monolith, isoproturon, stripping.

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ABBREVIATIONS

H_2S	Hydrogen sulphide
CO_2	Carbon Dioxide
SO_2	Sulphur dioxide
NH_3	Ammonia
MEA	Monoethanolamine
MDEA	n-Methyldiethanolamine
GLC	Gas Liquid Chromatography
aq.	Aqueous
org.	Organic
PTC	Phase Transfer Catalysis
3-AAP	3-aminoacetophenon
3-NAP	3-nitroacetophenon
H_2SO_4	Sulphuric acid
KIO_3	Potassium iodate
KI	Potassium iodide
$Na_2S_2O_3$	Sodium thiosulphate
FID	Flame ionization detector
TBPB	Tetrabutylphosphonium Bromide
T	Temperature
r	Rate of reaction

CHAPTER 1

1 INTRODUCTION

1.1 Sulfane

Hydrogen sulphide gas is a hazardous colourless gas with fetor rotten egg odour. Hydrogen sulphide is highly toxic & corrosive. It is also flammable & acerbic in nature. Volcanoes, Hot springs, cold springs emit some amount of hydrogen sulphide by hydrolysis of sulphide minerals.

$$MS + H_2O \rightarrow MO + H_2S$$

A very small amount of Hydrogen sulphide occur in rude petroleum on the other hand natural gas have extremely high H_2S content. Hydrogen sulphide is found in water too. A sulphate reducing bacteria produces usable energy under anaerobic condition i.e. in absence of oxygen by oxidizing sulphates to organic compounds, generating hydrogen sulphide as waste. A very small amount of hydrogen sulphide is formed in human body by bacterial breakdown of proteins containing sulphur in intestinal tract.

But now a days a considerable amount of H_2S is found in air due to human activity. So far petroleum refinery & natural gas extraction plants involves generation of maximum amount of hydrogen sulphide by hydrodesulphurization which liberates elemental sulphur by action of hydrogen. Other industrial sources of hydrogen sulphide are Coke oven plants, pulp & paper manufacturing, tanneries, waste water treatment, chemical manufacturing, textile manufacturing etc. The basic concept of generation of hydrogen sulphide in industry is contact of elemental sulphur with organic compounds at high temperature.

1.2 REASONS FOR TREATMENT OF SOUR GAS

Hydrogen sulphide has harmful effects on human. So it is advisable to treat sour gas from industrial gas stream. Some other reasons that induce the removal of hydrogen sulphide are

- H_2S gas is highly toxic. Its toxicity can be compared to carbon monoxide. It reduces to some other toxic gases like sulphur dioxide on ignition. It exists in other hazardous

forms like sulphite, thiosulfate etc. It's a reducing agent that forms complex with iron in mitochondria leading to prevention of cellular respiration.

- Hydrogen sulphide is flammable & explosive in nature. It is heavier than air. A mixture of air & hydrogen can be explosive. Hydrogen sulphide burns in presence of oxygen, with blue flame, to form sulphur dioxide & water.
- Hydrogen sulphide has very pungent smell. It causes irritation in eye, damage to nasal tract. It tends to settle down at the leakage site. So victim might be unaware of hydrogen sulphide presence which lead to knockdown.
- Hydrogen sulphide is corrosive in nature. So corrosion of pipelines & equipment's occur. It causes pitting & corrosion in waste water plant, sulphuric acid pitting in storage tank & high concentration may lead to corrosion of cement walls.
- Due to acidic nature of hydrogen sulphide, it causes deactivation of catalyst & side reactions. A high content of hydrogen sulphide in air may cause acid rain which possess a great environmental threat.
- Since elemental sulphur is not an economical product because cost of stripping is too much as well as an energy intensive process. Hence it is converted into some economical product having great commercial importance like pharmaceutical drugs.

For safety operation concerning hydrogen sulphide there are different standards of H_2S emission

- ✓ According to Occupational Safety & Health Administrations 10 ppm is the Permissible exposure limit time-weighted average for 8 hour per day.
- ✓ 100-150 ppm cause knockdown after few inhalations.

1.3 INDUSTRIAL PROCESS FOR THE REMOVAL OF H_2S

There are several industrial processes for removal of H_2S from gas stream like Claus process, Amine gas treatment, Ammonia based process, wet oxidation LO-CAT process etc.

1.3.1 Claus process

It can be abbreviated as absorption of hydrogen sulphide using aq. Alkanolamine. This is the most significant desulfurizing process in industry which helps in recovering elemental sulphur

from gaseous hydrogen. This desulfurizing process was first patented by Carl Friedrich Claus in 1883 which has become the industry standard after being modified by German company IG Farben. If the hydrogen sulphide content of the by-product gas derived from refining of crude oil or extraction of natural gas & other industrial processes is more than 25%, then suitable for recovery of elemental sulphur by Claus process.

The Claus process can be categorized into

a) **Thermal step**:-In this step the acid gas containing only combustible hydrogen sulphide is combusted substoichiometerically in presence of oxygen at a very high temperature of 850^0C. This is a highly exothermic free flame total oxidation of H_2S generating SO_2 that reacts away in subsequent reactions carried out in burner mufffle.

   $2H_2S + 2O_2 \rightarrow SO_2 + 2H_2O + S$ (combustion of hydrogen sulphide)

   The above shows that thermal step alone is responsible for conversion of two-thirds of hydrogen sulphide to elemental sulphur & rest to sulphur dioxide. Thermal step alone produces about 60-70% of the total amount of elemental sulphur produced.

b) **Catalytic step:-** This step involves three sub-steps: heating, catalytic reaction & cooling plus condensation. The product gas from burner is subjected to heating in a reheater at operating bed temperature of about 300 - 350^0C which prevents sulphur condensation on catalyst bed if not lead to catalyst fouling. Then the gas is subjected to series of catalytic converter. The high temperature in first bed helps to hydrolyze COS & CO_2. The catalytic conversion is maximized at lower temperatures but above the dew point of sulphur. The subsequent operating bed temperature for 2^{nd} & 3^{rd} bed is 240^0C, 200^0C respectively.

   $2H_2S + SO_2 \rightarrow 3S + 2H_2O$ (Claus reaction)

   The process gas stream coming from catalytic converter is cooled to 150-130^0C in sulphur condenser where steam is produced at the shell side of the condenser. Then the liquid sulphur is channelled to degassing unit to remove combustible gases from it &

elemental sulphur precipitates in the downstream. The elemental sulphur produced are in the form of S_6, S_7, S_8 & S_9.

Activated Al (III) or Ti (IV) oxide catalyst boost the sulphur yield in Claus reaction. Sulphur produced is further used in production of sulphuric acid followed by fertilizer, pesticides, pharmaceutical drugs & rubber products etc.

$10H_2S + 5O_2 \rightarrow 2H_2S + SO_2 + 7/2\ S_2 + 8H_2O$ (overall reaction)

However the Claus process has following disadvantages

- ✓ High operating temperature in thermal step consumes considerable amount of energy.
- ✓ For better yield the ratio of oxygen to H_2S must be controlled.
- ✓ Co_2 gas must be removed from the by-product gas before Claus step.
- ✓ Stripping of sulphur from Aq. Ethanolamine is costly.
- ✓ The elemental sulphur is not a good product from economical point of view

Later modified Claus process was patented but this process is used for gas stream containing more than 50% hydrogen sulphide & recovers about 94-97% sulphur.

Advantages of Aq. Alkanolamines in gas treating:-

- MDEA is a tertiary amine, is less basic & can be used in significantly higher concentration because it has a greater capacity to react with acid gas.
- It is selective in nature. It reacts with all the H_2S but a part of CO_2 but other alkanolamines reacts with all H_2S & all CO_2.
- Due to its product selectivity, it converts only one type of reactant to product most out of ortho, para & meta.
- Due to increased capacity the capital cost is decreased.
- Lower Energy cost & higher selectivity compared to primary & secondary amines.
- MDEA delivers energy saving from reduced reboiler duties & lower overhead condenser duties.
- MDEA has very less corrosivity compared to MEA & DEA.
  Corrossivity of amines MEA>>DEA>>MDEA.

1.3.2 Ammonia based process

Utilization of aq. Ammonia in the elimination of hydrogen sulphide from by-product gas stream had been well practised by Hamblin, Harvey & Makrides. There are two scrubber units. The gas stream consisting of hydrogen sulphide & NH_3 enters the first scrubber where water is sprayed from top to absorb ammonia from the gas. Then in the following scrubber H_2S is removed. The solution obtained in the first scrubber becomes the absorbent for second scrubber. Then in the second scrubber ammonium sulphide is formed & sent to deacidifier which separates ammonium sulphide to form H_2S rich vapour & liquor rich NH_3. This process has declined over a decade but still used in coke oven units. The reactions happening in the system are:

$NH_3 + H_2O = NH_4OH$

$NH_3 + H_2S = NH_4HS$

$2NH_3 + H_2S = (NH_4)_2S$

The NH_3-based methodology is suitable for gas streams including both H_2S and NH_3 ,as synchronous removal of NH_3 is evident in this procedure. Moreover, for the gas streams containing both H_2S and NH_3, the removal of both impurities may be completed in a single step in the alkali based process rather than two stages as in the circumstance of alkanolamine-based methodology.

Advantages of Ammonia based process

The absorption of hydrogen sulphide in weak alkaline solution is faster compared to CO_2 because the absorption of carbon dioxide into weak alkaline solution is liquid film controlled whereas for hydrogen sulphide absorption rate is gas film controlled. Hence H_2S gets absorbed into aq. Ammonia solution is fast & reliant upon concentration of NH_3 in the aq. Solution. So the use of aq. Ammonia solution enhances selective absorption of H_2S or CO_2. For selective absorption of H_2S from a mixture of CO_2 & H_2S spray column is used.

Disadvantages of ammonia based process:-

There is another water wash step involved after ammonia scrubbing step to remove ammonia from the treated gas stream to reduce the partial pressure of ammoniar. The cost of regeneration hikes as the process is carried out at high temperature.

The scrubbing step involves the use of soluble catalysts. Hence the sulphur product gets contaminated.

1.3.3 Wet oxidation LO-CAT Process:

The Lo-CAT process is modified Claus process patented in 1980. It's a wet scrubbing liquid redox system that uses iron as catalyst in chelated organic solution to oxidise hydrogen sulphide to innocuous elemental sulphur by reduction of iron ferric to ferrous. The organic chelating solution is used to prevent iron sulphide/ iron hydroxide. The ferric iron is sent to oxidizer from absorber where it oxidises to ferrous ion by atmospheric oxygen. This process does not involve use of any toxic chemicals & also does not produce any hazardous chemicals. The reactions steps involved in LO-CAT processes are

- Absorption of hydrogen sulphide gas

  $H_2S(g) + H_2O(aq.) \leftrightarrow H_2S(aq.) + H_2O(aq.)$
- Ionization of aq. hydrogen sulphide

  $H_2S(aq.) \leftrightarrow H^+ + HS^-$
- Sulphide oxidation

  $HS^- + 2Fe^{3+} \leftrightarrow S^0 + 2Fe^{2+} + H^+$
- Absorption of oxygen

  $1/2O_2(g) + H_2O(liq.) \leftrightarrow 1/2\ O_2(g) + H_2O(aq.)$
- Iron oxidation or regeneration of catalyst

  $2Fe^{2+} + 1/2O_2(aq.) + H_2O \leftrightarrow 2Fe^{3+} + 2OH^-$

Advantages of LO-CAT process:-

- ✓ This process does not produce any hazardous chemical substance.
- ✓ This is a well-developed economically fit process in industry for last 35 years.
- ✓ When H_2S exceeds a certain level sulphur abatement systems are often needed which are quite expensive. The LO-CAT process is substitute for it.

- ✓ This method provide certain amazing features like 100% turndown, single stage removal efficiencies in excess of 99.9% and can treat any gas stream containing H_2S.

1.3.4 Sulferox Process

This method is a shell proprietary iron redox process similar to modified Claus process. Sour gas stream is brought into contact with a liq. containing soluble Fe^{3+}. Hydrogen sulphide is oxidized to elemental sulphur & Fe^{3+} to Fe^{2+}. The system regenerates catalyst by oxidation with air & sulphur is recovered from the solution.

1.3.5 CrystaSulf Process

This process was patented in 1990 by The Gas Research Institute for removal of hydrogen sulphide from high pressure gas. It uses a non-aq. Solution with a high solubility for elemental sulphur. CrystaSulfa process avoids aq. Sulphur recovery by direct treatment of high pressure sour gas.

1.4 Kipp's process (Laboratory Scale)

Hydrogen sulphide can be prepared by Kipps process on laboratory scale using Kipps apparatus. Kipps apparatus is a combination of two vertically stacked cylinders with base as a third flat cylinder either made up of glass or fibre. A conical tube connects top & bottom cylinders. Stopcock is attached at the middle cylinder & another hole is attached at the bottom cylinder for quick assault of unreacted acid. To stop the reaction stopcock is stooped. Increase in pressure in middle cylinder due to unreleased H_2S gas, expels acid back to top cylinder. The solid used is FeS which is insoluble in acid.

The FeS sticks are put in the middle cylinder. Then sulphuric acid is poured in the top cylinder. Then acid directly flows down to bottom cylinder to fill it. Then extra acid start flowing to middle cylinder by thrusting FeS sticks. Thus H_2S is prepared in lab by following reaction

$FeS + H_2SO_4 \rightarrow H_2S + FeSo_4$

The sulphide concentration can be determined by iodometric titration, is a volumetric redox titration here appearance or disappearance of iodine indicates end point.

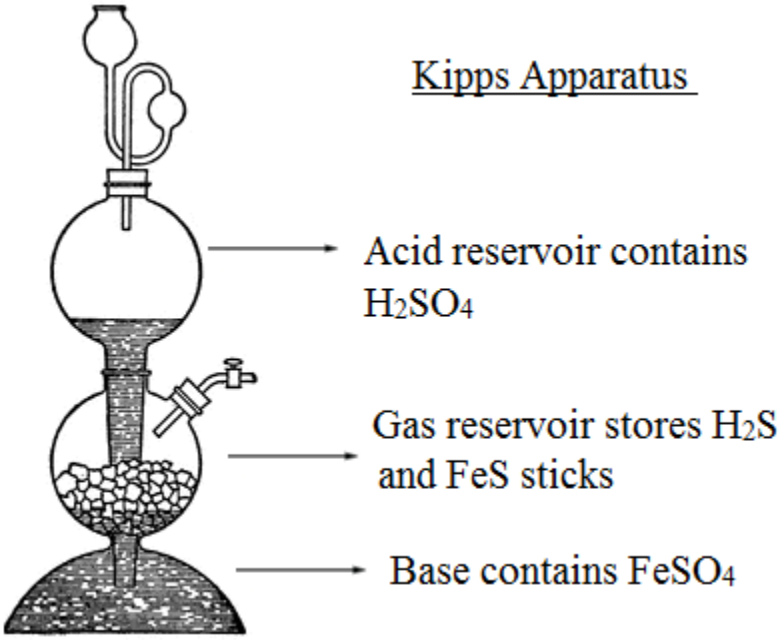


Figure 1.2 Kipp's Apparatus

1.5 Phase Transfer Catalyst

1.5.1 PTC

Phase transfer catalysis is a special form of heterogeneous catalysis in which, reaction occurs by phase transfer catalyst (PTC) between two reactants. One of the reactant (normally ionic) often soluble in aqueous phase but insoluble in organic phase but the other reactant is soluble in organic phase but insoluble in aqueous phase.

PTC facilitates migration of anion (from the reactant) from aqueous phase to organic phase where reaction can occur with other reactant. It obtains higher yields, helps to achieve faster reaction, make fewer by products etc.

PTC are especially useful in green chemistry — by allowing the use of water, the need for organic solvents is reduced.

ADVANTAGES OF USING PTC OVER CONVENTIONAL PROCEDURE

- Are fast & don't require vigorous conditions.
- Higher yield & less by product.

- Reaction usually occurs at low temperature.
- The reaction which don't proceed normal way can be made to proceed in good yield.
- PTC are useful in green chemistry.

Choice of PTC

Phase transfer agent must be cationic & have enough organic structure to be able to partition with nucleophilic anion in the organic phase. In simple term cation – anion bond should be loose enough to ensure anion reactivity. The cation part must be highly lipophilic for high compatibility with organic phase.

1.5.2 MECHANISM OF PT CATALYSIS

PTC ($Q^+ X^-$) functions as a vehicle to transfer the anion (Y^-) of metal salt ($M^+ Y^-$) from one phase to organic phase where it reacts with substrate RX giving desired product RY & regenerating $Q^+ X^-$ to continue PTC cycle.

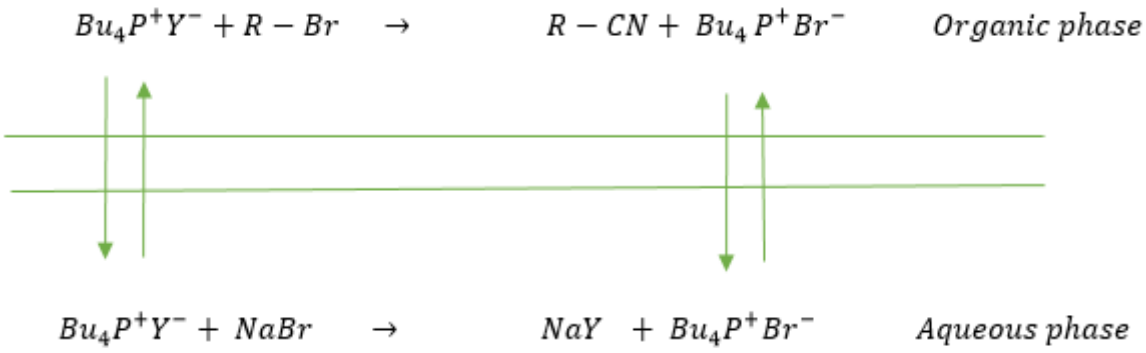


Fig 1.3 Overview of PTC mechanism

Factors that affects mechanism of PTC

- The reaction becomes faster as interfacial area increases.
- Rate of transfer slows down with the size o alkyl group RN^+.

- Large weakly hydrated or organic liquids (like iodine per chlorate) are easily transferred while small hydrated anions (fluorides, hydroxides) are poorly transferred.

1.6 CLASSIFICATION OF PTC

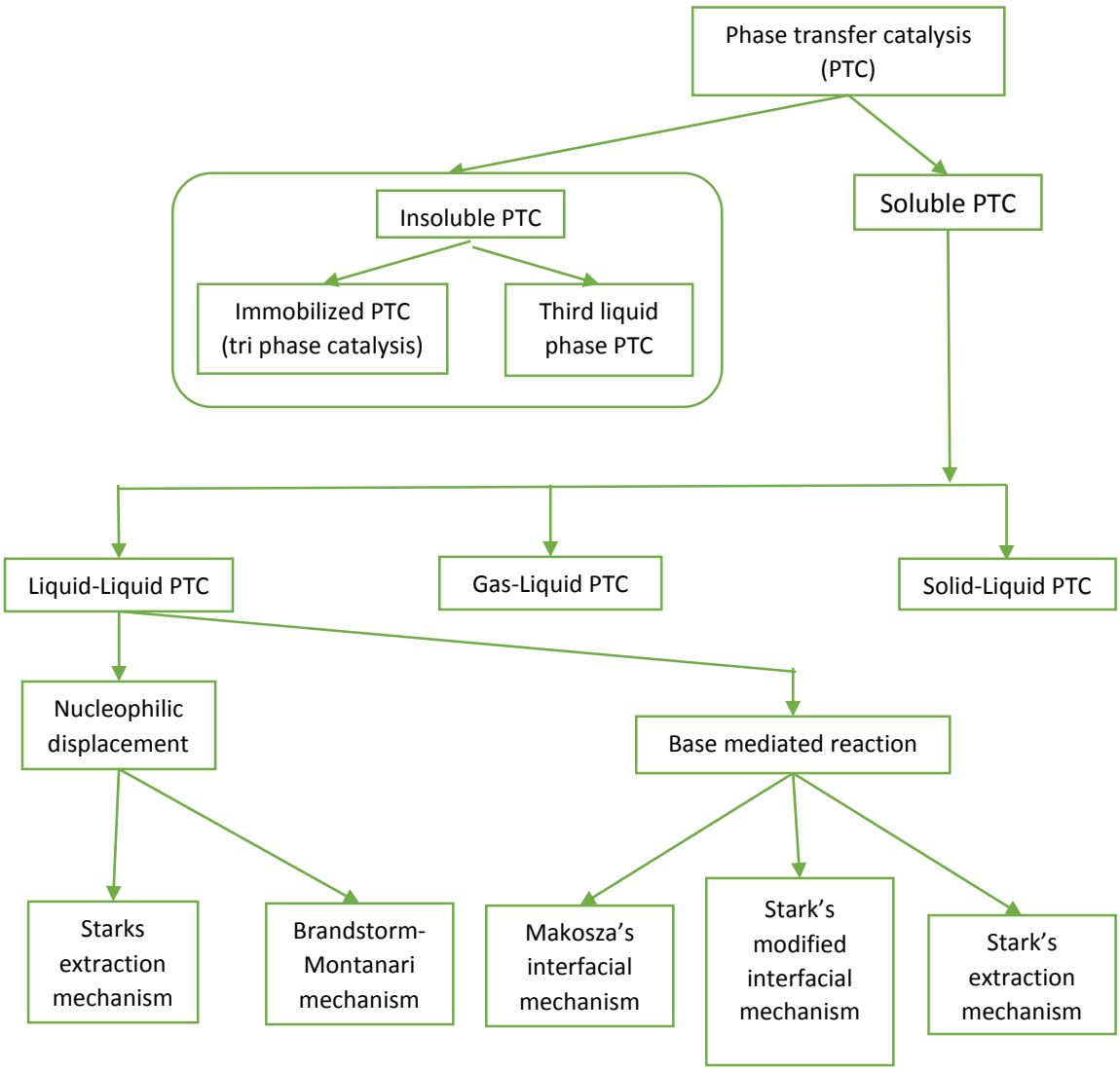


Fig 1.4 Classification of phase transfer catalysis

1.6.1 SOLID – LIQIUD PTC

- **Homogeneous Solubilization**

It was proposed by Melville & Goddard in 1988. From the name itself the procedure can be imagined. Here the nucleophilic solid have finite solubility in organic phase. So it reacts directly with inorganic salt in organic phase. The dissolved MY_{org} reacts with quaternary salt QX_{org} giving QY_{org} in organic phase which reacts with reactant RX_{org} to give product RY_{org} & regenerating catalyst QX_{org}. Here both quaternary ammonium salt & nucleophile are soluble in organic phase. Hence it is called homogeneous solubilisation.

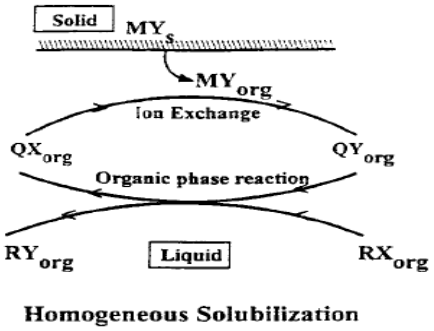


Fig 1.5 Mechanism of homogeneous solubilization

- **Heterogeneous Solubilization**

It was proposed by Naik & Doraiswamy in 1997. Here the nucleophile is insoluble in organic phase but quaternary ammonium salt is soluble in organic phase. In this method quaternary salt or nucleophilic anion comes to the interface of organic phase & solid i.e. solid crystalline lattice by phase transfer catalyst. The QX_{org} reacts with the MY_s at solid crystalline lattice giving QY_{org} to organic phase which further reacts with reactant RX_{org} giving product RY_{org} & regenerating catalyst QX_{org} .

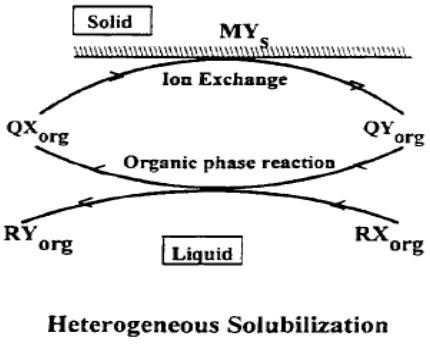


Fig 1.5 Mechanism of heterogeneous solubilisation

1.6.2 LIQUID – LIQUID PTC (nucleophilic displacement)

- **Starks extraction mechanism**

Here Q^+ is soluble in both organic & aqueous phase. Hence the phase transfer catalyst Q^+X^- can move freely between both phases. Q^+X^- reacts with metal or inorganic salt generating Q^+Y^-. Then it moves to the organic phase & reacts with reactant RX generating product RY & regenerating catalyst Q^+X^-. Here tertiary ammonium salt acts as a vehicle to transfer nucleophile of metal salt from aqueous phase to organic phase.

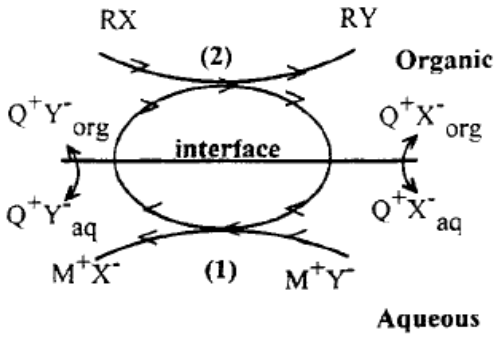


Fig 1.6 Starks extraction mechanism

- **Brandstorm's interfacial mechanism**

Sometimes the quaternary salt could be too lipophilic to dissolve in aqueous phase i.e. Q^+ is insoluble in aqueous phase yet functions as a very good phase transfer catalyst. In this case the PT catalyst reside in organic phase but anion exchange occurs at interface of organic & aqueous phase. Here Phase Transer catalyst $Q^+X^-_{org}$ reacts with metal salt M^+Y^- at interface generating $Q^+Y^-_{org}$ & M^+X^- at interface. Then Q^+ acts as a vehicle to carry nucleophile from metal salt from interface to organic phase. $Q^+Y^-_{org}$ reacts with reactant RX giving product RY & regenerating catalyst $Q^+X^-_{org}$.

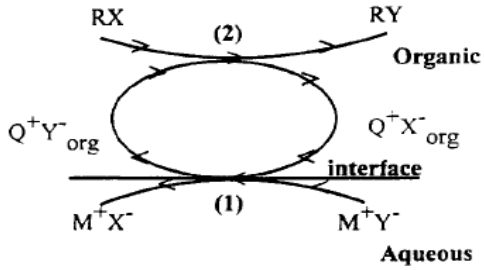


Fig 1.7 Brandstorm's interfacial mechanism

- **Makosza's interfacial method**

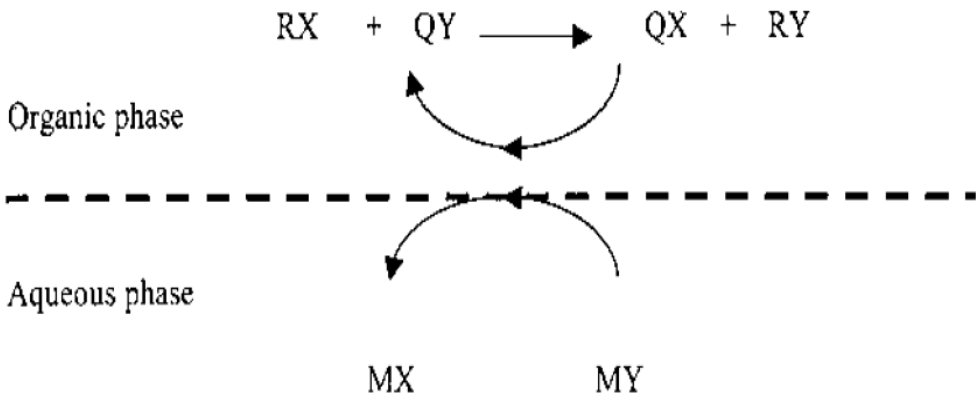


Fig 1.8 Makosza's interfacial mechanism

1.6.3 GAS – LIQUID PTC

GLPTC are carried out in a thermostatized glass column containing a solid bed consisting of a solid salt of nucleophile or of a base able to generate it & catalyst adsorbed on solid.

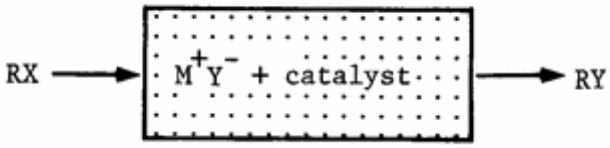


Fig 1.9 Gas –Liquid PTC

1.6.4 REVERSE PTC

A cationic reactant in the aqueous phase is continuously transferred into the organic phase in the form of a lipophilic ion pair with a lipophilic, non-nucleophilic anionic catalyst, and reacts with the second reactant in the organic phase.

1.6.5 INVERSE PTC

It is reasonable to expect that PTC reactions can also be performed by transferring the organic reactants from the organic phase into the aqueous phase for reaction with a second reactant.

1.7 Classification of catalyst

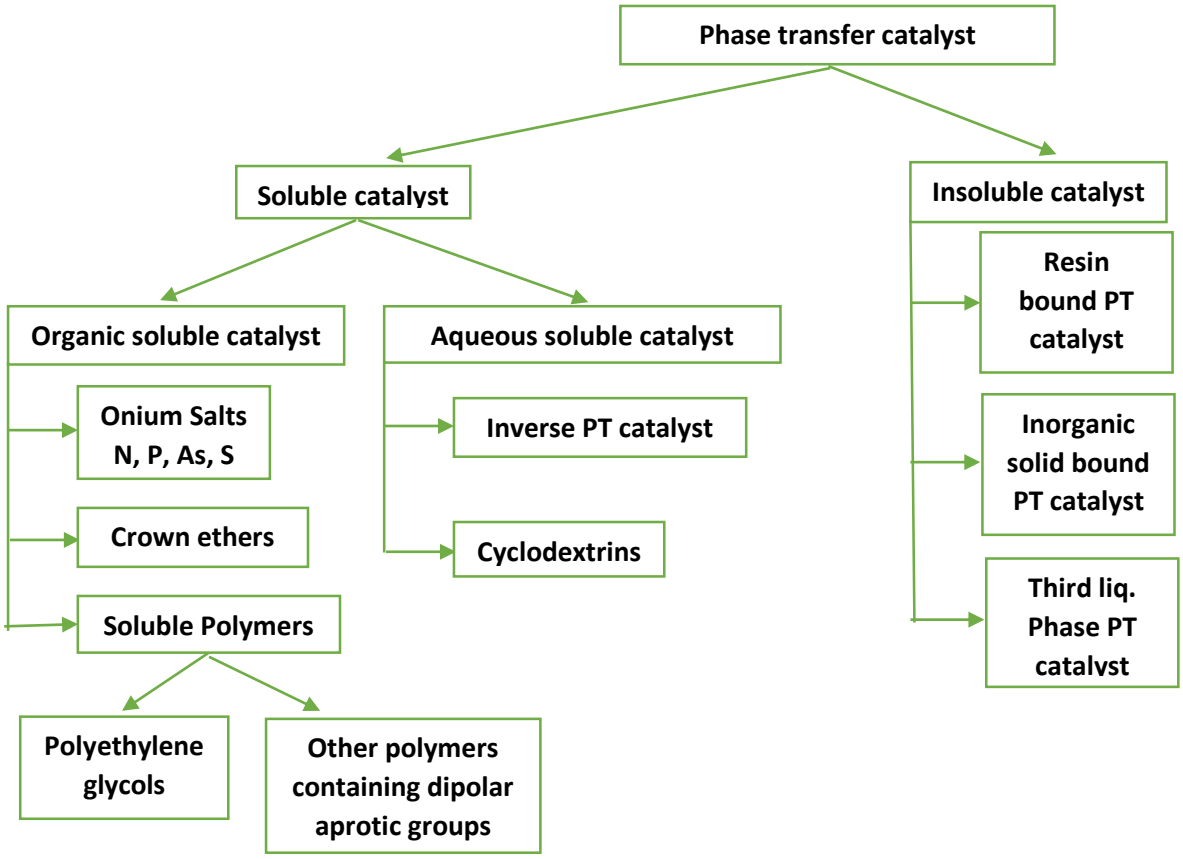


Fig 1.10 Classification of catalyst

Catalyst	Cost	Stability & Activity	Use & Recovery
Ammonium salts	cheap	Moderately stable up to 100°C. Moderately active.	Widely used. Relatively difficult recovery.
Phosphonium salts	Costly	More stable thermally than ammonium salts, although less stable under normal conditions	Widely used. Relatively difficult recovery.

Crown ethers	Expensive	Stable and highly active both under normal conditions and up to even 150-200°C.	Widely used. Relatively difficult recovery.
Cryptands	Expensive	Stable and highly reactive, in absence of strong acids.	Higher reactivity increases usage in spite of high costs and toxicity.
PEG	Very cheap	More stable than quaternary ammonium salts, but lower activity.	Often used. Relatively easy to recover.

Table 1.1 Details of some commonly used catalyst

1.8 Details of chemical substance Used in Present work

1.8.1 REACTANT

3-nitroacetophenon

Formula: $C_8H_7NO_3$

Molecular weight: 165.15 g/mol

MP: 76-78^{0}C

BP: 202^{0}C

It is white to light pale brown in colour, insoluble in water.

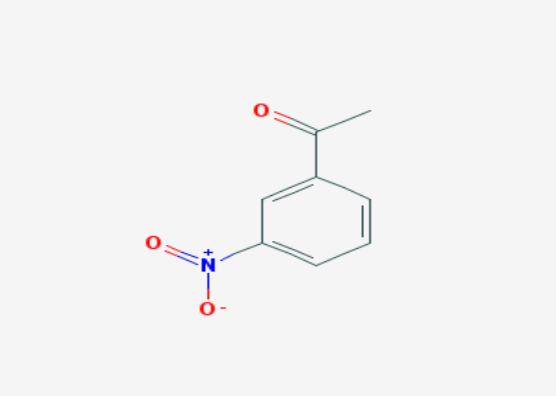


Fig 1.11 3-NAP

1.8.2 PRODUCT

3-aminoacetophenon

Formula: C_8H_9NO

Molecular weight: 135.16 g/mol

MP: 94-98^{0}C

BP: 290^{0}C

It is yellow to light brown crystalline powder.

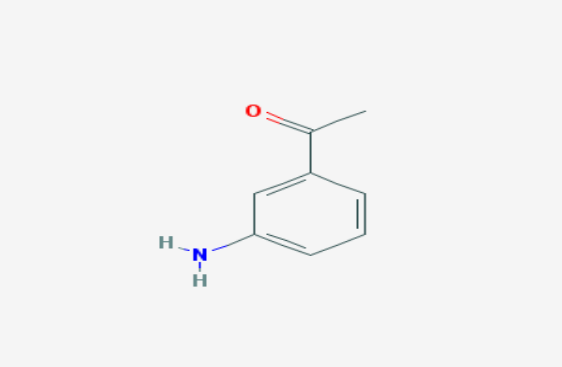


Fig 1.12 3-AAP

USES:

- Potential antibacterial property
- Synthesis of HIV-1 integrase inhibitors
- Synthesis of pectamycin & other pharmaceutical products
- Synthesis of new catalyst
- Manufacture of silica monolith
- Bee repellent
- Spectrophotometric determination of isoproturon

1.8.3 SOLVENT

Methyldiethanolamine

Formula: $C_5H_{10}NO_2$

Molecular weight: 119.162 g/mol

MP: -21^{0}C

BP: 247.1^{0}C

Viscosity: 101mPa at 20^0C

It is a colourless liquid with amine like odour. It is miscible with benzene & water.

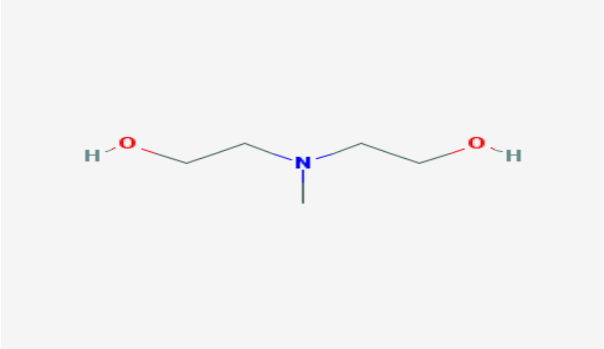


Fig 1.13 n-Methyldiethanol amine

1.8.4 CATALYST

Formula: $C_{16}H_{36}BrP$

Molecular weight: 339.334 g/mol

MP:100-103^0C

It is a clear to yellowish jelly type liquid. Soluble in water.

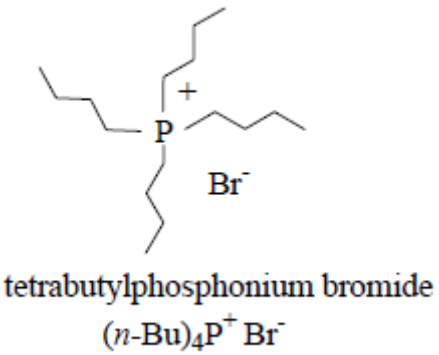


Fig 1.14 Tetrabutylphosphonium bromide

CHAPTER 2

2 Literature review

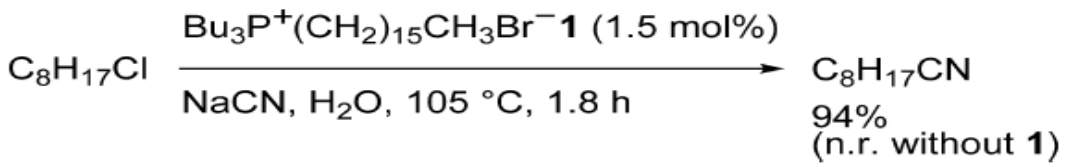
2.1 Use of aqueous Alkanolamine for removal of H_2S

Recovering of hydrogen sulphide from the by-product gas stream by ammonium hydroxide was patented by Kohl & Nielsen, 1997. Hamblin, 1973 modified this process further for removal of H_2S from gas streams converting ammonium hydroxide to produce ammonium hydrosulphide. Further it was oxidised to get ammonium polysulfide in the effluent stream. Elemental sulphur can be recovered by treating ammonium polysulphide stream. Recently simultaneous absorption of H_2S & ammonia into water in an agitated vessel having a flat interface was patented by Asai et al (1989). Rumpf et all. (1999) verified simultaneous absorption of hydrogen sulphide & ammonia for a typical range of pressure up to 0.7Mpa & temperature varying from 313-393K.

Now a days aqueous alkanolamines are used broadly for recovering of H_2S & CO_2 in various gaseous stream of refineries which is the process with upmost commercial importance. In chapter-1 it was briefly discussed. Different types of research works are going on treatment of acid gas or specifically sour gas.

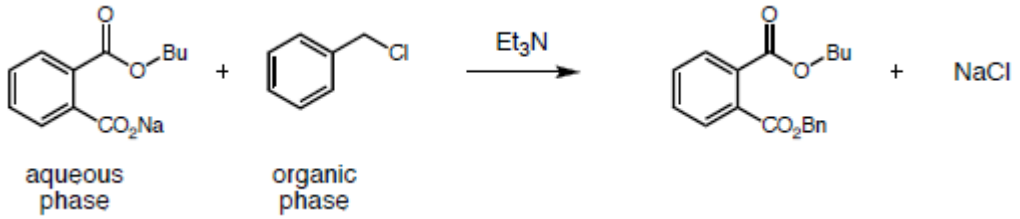
2.2 Phase transfer catalysis

Starks in 1971 introduced phase transfer catalysis into chemistry to explain crucial role of quaternary ammonium or phosphonium salts when two heterogeneous immiscible reactants react being in two separate phases.



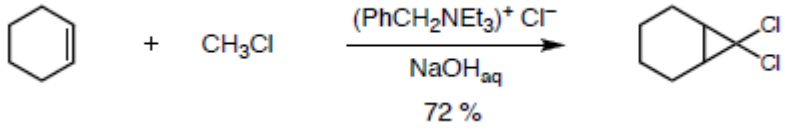
The key element of this particular, specific method is reactivity of quaternary phosphonium cyanide which moves freely between both phases & sufficiently nucleophilic to make the reaction happen.

In 1946 for first time commercial use of PTC was carried out.



For first time benzyltriethylammonium chloride is used as phase transfer catalyst to manufacture by addition of trimethylamine as aq. Phase.

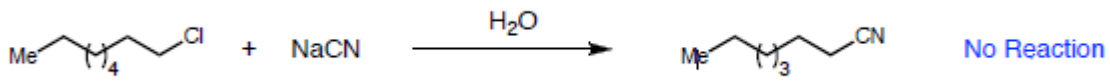
For first time a mechanistic model was proposed on PTC by M. Makosza (1969).



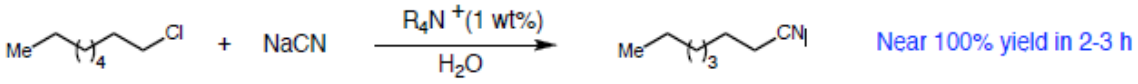
Makosza postulated an mechanistic model for ion exchange between the tetraalkylammonium chloride and aq. NaOH to form the base that reacts quite effectively in the organic phase.

In 1971 the concept of PTC was described by C.M. Starks (1971).
In 1984 for first time example of an asymmetric PTC was patented by Merck Process.

A phase transfer catalyst is a catalyst which facilitates the migration of a reactant in a heterogeneous system from one phase into another phase, mostly from aq. Phase to organic phase, where reaction can take place. Ionic reactants are often soluble in an aqueous phase but are insoluble in an organic phase. If the phase transfer catalyst is present the reaction will happen.
Phase transfer catalysis or PTC, reaction is accelerated by the phase transfer catalyst.
PTC for anions reactant are often quaternary ammonium salts. PTC for cations are often crown ethers.



This reaction won't happen cause 1-chloronate & sodium cyanide form two separate layers.



When an appropriate quaternary ammonium salt is added, tetrahexylammonium chloride, the displacement occurs rapidly with a yield of 100% in 2-3 hrs.

In this process ammonium salt catalyst

1) Transfers the cyanide into the organic phase.

2) Activates the transferred cyanide for the reaction with the alkyl halide to organic phase.

3) Transfers the displaced chloride anions back to the aqueous phase i.e. regeneration of catalyst to start a new catalytic cycle.

Effects of variations on PTC reactions

- Agitation Influence only the transfer rate
  - Agitation speed should be high enough so that it has no influence on the overall reaction rate.
- Organic solvents can greatly influence the intrinsic reaction rate
  - Affect the interfacial tension which influences the transfer rate
- Temperature
  - Most quaternary ammonium salts decomposes at higher temperature, for examples 50-70 ºC for systems containing KOH
  - CH2Cl2 is used extensively because of it dissolves most quaternary salts and is also hydrophobic
  - For asymmetric PTC non-polar solvents such as toluene are used extensively because they maximize the interactions between the two counter ions.

Can greatly influence the intrinsic reaction rate

- Co-catalyst

– Often used to help one of the two steps. For example, addition of alcohols, particularly diols, Significantly increase the ease of hydroxide anion transfer

Can influence both steps

- Catalyst

– The size and shape affect the anion activation

The most important variable

Intrinsic reaction rate

– Ability to solubilize the aqueous phase reagent into the organic phase Transfer rate

– Bulkiness can slow the transfer rate (as seen earlier)

– The stability of the catalyst under the reaction conditions

– The surfactant property of the catalyst Transfer rate

2.3 Conclusion

There is no particular papers on PTC industrial uses for different treatments. The recovering of hydrogen sulphide is patented very nicely. There are lot of kinetic models to explain PTC like nucleophilic substitution & interfacial mechanism. Till now no attempt has been made to synthesize 3-AAP from 3-NAP in H_2S rich MDEA solution using TBPB as catalyst.

2.4 Objective of the project

The present study is to optimize the utility of hydrogen sulphide found in various gas streams with an effective, economical process than Claus's method. The aim of the project is to study the reduction of 3-nitroacetophenon to 3-aminoacetophenon by phase transfer catalysis method using H_2S rich n-methyldiethanolamine as aq. Phase & tetrabutylphosphonuim bromide as phase transfer catalyst.

The present research is focused on

- ✓ Synthesis of fine chemicals like 3-AAP using H_2S rich aq. MDEA in presence of phase transfer catalyst TBPB.
- ✓ Effect of different types of process variables like temperature, stirring speed, catalyst loading, concentration of reactant & elemental sulphur loading on 3-NAP, selectivity of products & kinetics of reaction.
- ✓ Determining a suitable mechanism of reaction from variation of reaction rate & other process parameters.
- ✓ Bargain a suitable commercially important method & appropriate conditions from study of all types of process variables.

CHAPTER 3

3 Experimental

3.1 Chemicals & Catalyst

H_2S is prepared in the laboratory using Kipp's apparatus. The description of apparatus is given in. Distilled water used here is prepared by deionization in quartz distillation unit.

- Chemicals brought from Merck (India) Ltd. Mumbai
  Toluene (≥ 99.5%) of analytical grade; 3-nitroacetophenon, TBPB; MDEA (≥ 98%) synthesis grade; the chemicals used for iodometric titration for estimation of sulphide content i.e. sodium thiosulfate, potassium iodide, potassium iodate, sulphuric acid, sodium hydroxide pellet & starch of analytical grade .
- Chemicals ordered from Sigma Aldrich Mumbai India
  Sulphur, Iron (II) sulphide sticks (FeS)

3.2 PREPARATION OF H_2S RICH AQ. N-METHYLDIETHANOLAMINE

H_2S is prepared in laboratory scale by reacting FeS sticks with 1 molar H_2SO_4 in Kipp's apparatus. The stopcock attached at middle cylinder is connected to one end of the pipe of small diameter & the other end is inside a 250ml gas bubbler containing MDEA solution. The H_2S gas pass through the pipe & is bubbled in MDEA solution for 8-10 hrs according to the sulphide concentration required or till the bubbling ceases. The concentration of MDEA solution is 30-35%, prepared by diluting suitable amount of MDEA solution in distilled water. Another similar pipe is extended from MDEA solution in 250ml bubbler to atmosphere to maintain pressure gradient for H_2S bubbling.

The reaction between MDEA & H_2S is exothermic in nature. Hence the gas bubbler is immersed in water bath full of ice to prevent disulphide formation via oxidation of sulphide. Then the H_2S rich MDEA solution is subjected to iodometric titration to determine the sulphide concentration.

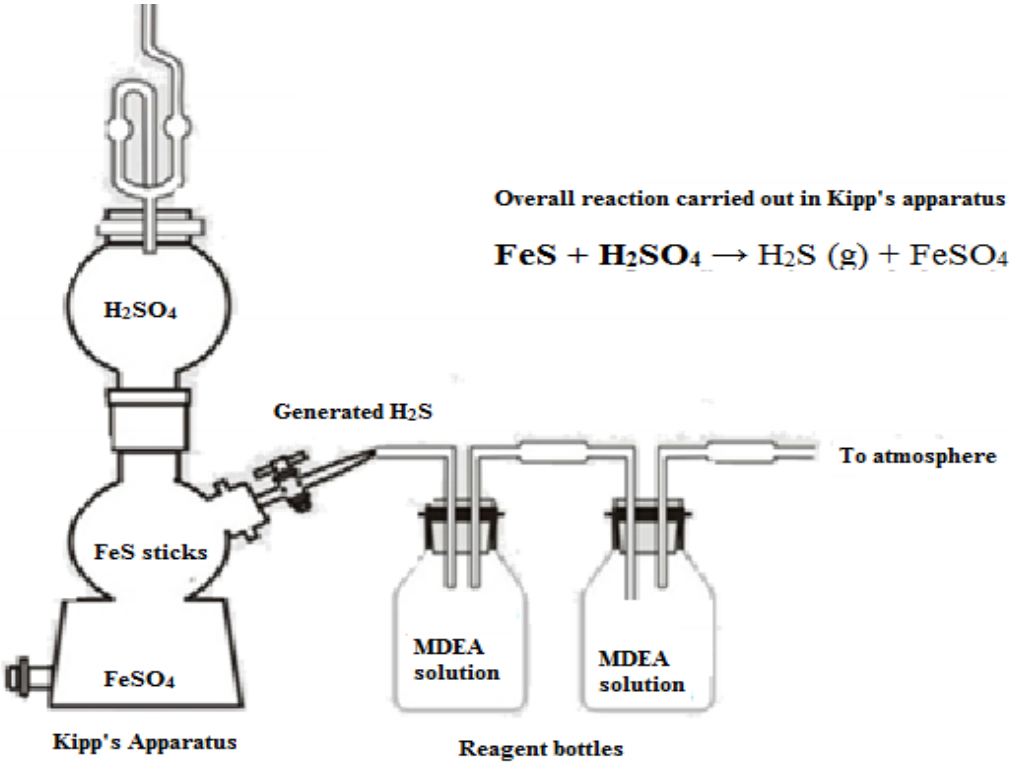


Fig 3.1 Kipp's Apparatus with MDEA

3.3 DETERMINATION OF SULPHIDE CONCENTRATION

3.3.1 STANDARDIZATION OF THIOSULPHATE SOLUTION

Iodometric test is performed to determine the sulphide concentration.

- **Preparation of standard (0.025 M) KIO_3 solution**: 0.428 gm of KIO_3 was weighed accurately and dissolved in distilled water & made up to 100mL in a graduated volumetric flask.

- **Preparation of standard (0.1 M) sodium thiosulfate solution:** 25 gm of $Na_2S_2O_3.5H_2O$ crystals was weighed and made up to 1 L in a graduated volumetric flask by dissolving in distilled water. About 0.1 g of sodium carbonate or three drops of chloroform was added to this solution to keep the solution for more than a few days.

- **Standardization of sodium thiosulfate solution by standard KIO_3 solution**: 25 mL of 0.025M KIO_3 solution was taken and 1 gm (excess) of potassium iodide (KI) was added to it. About 3 mL of 1 M H_2SO_4 was next added to the solution. The iodine (I2) liberated due to reaction

$$\boldsymbol{KIO_3 + 5KI + 3H_2SO_4 \rightleftharpoons 3I_2 + 3H_2O + 3K_2SO_4}$$

Was titrated with 0.1 M thiosulfate solution. When the colour of the solution turns pale yellow, distilled water is aded to dilute it to 200 mL. 2 mL of starch solution was added and the titration is continued until the colour changes from blue to colourless. The chemical reaction involved in this titration is given below

$$\boldsymbol{2Na_2S_2O_3 + I_2 \leftrightharpoons Na_2S_4O_6 + 2NaI}$$

Therefore, 1 mole of $KIO_3 \equiv 3\times2$ mole of $Na_2S_2O_3$

$$\therefore Strength\ of\ thiosulphate\ solution = \left(\frac{6 * strength\ of\ KIO_3 * volume\ of\ KIO_3}{volume\ of\ thiosulphate\ consumed}\right)$$

3.3.2 ESTIMATION OF SULPHIDE CONCENTRATION

- **Preparation of 10 M NaOH:** About 40gms of NaOH was taken & made up to 100 mL by adding distilled water in a conical flask.
- **Preparation of 5% KI solution:** 5 gm of KI was taken in a conical flask & made up to 100ml by adding distilled water.
- **Preparation of 4 M H_2SO_4 solution:** 23.1 mL of H_2SO_4 was taken in a flask & made up to 100 mL by adding distilled water.
- **Preparation of 0.2% Starch solution:** 100 mL of distilled water was boiled. About 0.2 gm of starch powder was added to boiled water & again boiled for 1 min. Then the solution was cooled by tap water followed by fridge. About 2.5 gm of KI was added to it after cooling.

3.3.2.1 Iodometric Titration

Iodometric titration is a volumetric analysis, a redox titration where appearance or disappearance iodine indicates the end point.

$$\therefore \mathbf{2}\boldsymbol{I}^{-} = \boldsymbol{I}_{\mathbf{2}} + \mathbf{2}\boldsymbol{e}^{-}$$

$$\mathbf{4}\boldsymbol{IO}_{\mathbf{3}}^{-} + \mathbf{6}\boldsymbol{OH}^{-} + \mathbf{3}\boldsymbol{S}^{\mathbf{2}-} = \mathbf{3}\boldsymbol{SO}_{\mathbf{4}}^{\mathbf{2}-} + \mathbf{4}\boldsymbol{I}^{-} + \mathbf{6}\boldsymbol{H}_{\mathbf{2}}\boldsymbol{O}$$

$$4\ mole \text{ of } IO_3^- = 3\ mole\ of\ S^{2-}$$

$$\therefore H_2S\ concentration = \left\{\left[(15 * S_{iodate}) - \frac{\left(V_{thiosulphate} * S_{thiosulphate}\right)}{6}\right] * \frac{3}{4} * \frac{N_d}{10}\right\}$$

Where S_{iodate} = strength of KIO_3

$V_{thiosulphate}$= Volume of thiosulphate

$S_{thiosulphate}$= strength of thiosulphate

N_d = No. of times of dilution

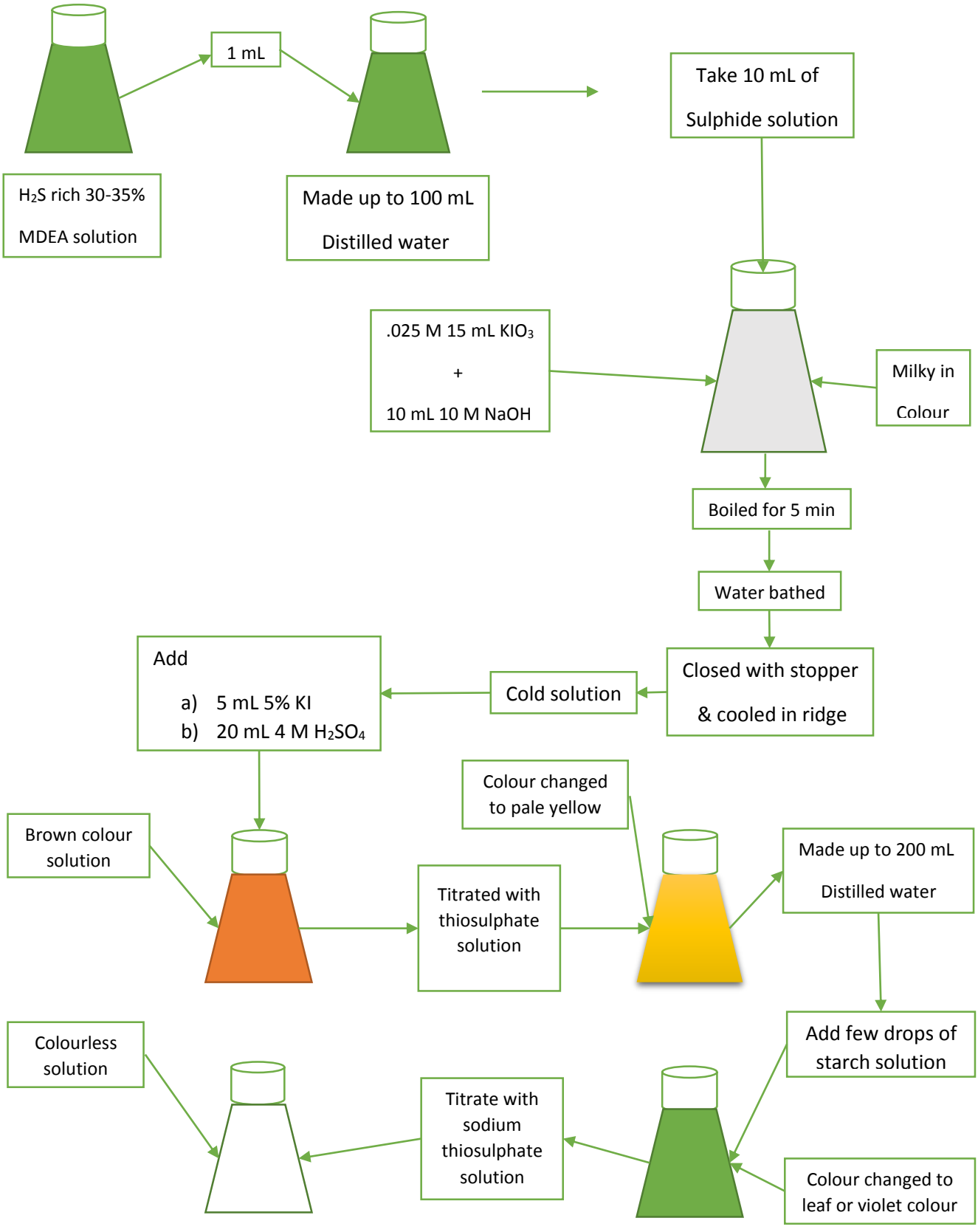
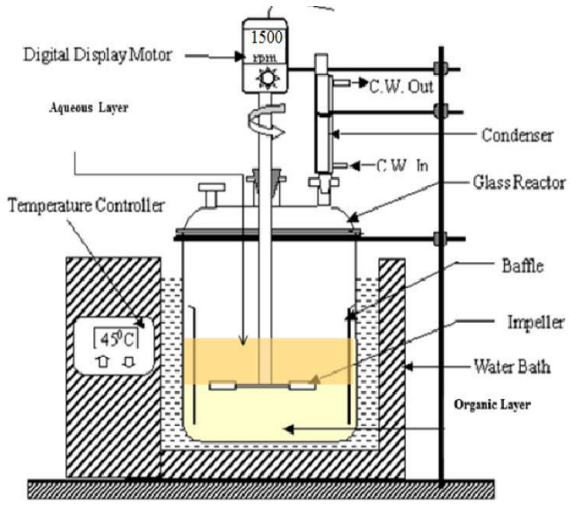


Fig 3.2 Schematic procedure of iodometric titration

3.4 Reactor setup

The design of a typical reactor is as shown in the fig. All the reactions are to be carried out in a thermostatic (± 0.5 0C) three-necked 250-ml (6.5 cm I.D.)in a batch mode equipped in a fully baffled mechanically stirred glass reactor. The reactor is mechanically agitated using a 2.0 cm-diameter six-bladed glass disk turbine impeller the speed of which can be regulated manually. The blades of the stirrer are positioned at a height of 1.5 cm from the bottom which ensures efficient stirring of the reaction mixture. Borosilicate glass beaker would be used as the contactor and three-necked flask, a dropping funnel serving the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding the feed. The motto is to reduce the building up of mass transfer resistance. This arrangement ensures excellent solid-liquid mixing for high mass transfer rate. The reactor assembly is to be kept in a constant temperature water bath whose temperature could be controlled within ± 0.5 0C and mechanically stirred at a known speed with an electric motor.



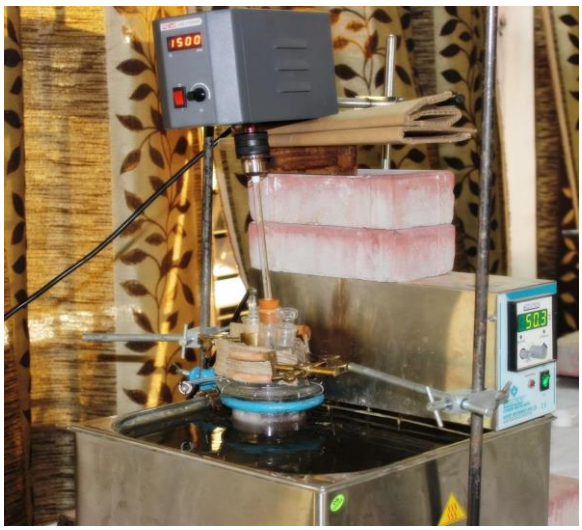


Fig 3.3.1 Front view of a typical reactor Fig 3.3.2 Top view of a typical reactor

3.5 Reaction procedure

Reaction procedure for 3-AAP

- H_2S gas was prepared in the laboratory using Kipp's apparatus followed by absorption in MDEA solution. The concentration of MDEA solution taken was 30-35% by adding required distilled water.
- Iodometric titration was performed to determine the sulphide concentration of the prepared solution.
- Organic phase was prepared by adding toluene to 4.5 gm of 3-NAP & volume made up to 30 mL of toluene followed by addition of 0.45 gm 0f TBPB.
- Aqueous phase was prepared by dissolving 0.3 gm of elemental sulphur in 30 mLof H_2S rich MDEA solution.
- The aqueous phase was fed into the reactor first followed by organic phase & catalyst TBPB.
- The reactor was immersed in an isothermal water bath & the temperature was maintained at 50^0C.
- The stirring speed was gradually increased to 1500RPM.
- Each time the experiment carried out, at least 9 samples of volume 0.4 mL organic phase collected carefully by pippete at 10min, 15min, 30min, 60min, 120min, 240min, 360min, and 480min.
- For temperature variation, four experiment were carried out at 313K, 323K, 333K & 343K.
- For stirring speed variation, experiment was carried out for 500, 800, 1000, 1500, 2000 & 2500 RPM.
- For reactant concentration variation, experiment was carried out at 1.5 gm or 0.3027 mol/lit, 3gm or 0.6055 mol/lit, 4.5gm or 0.9082 mol/lit, 6gm or 1.21 mol/lit.
- For sulphide concentration variation, experiment was carried out at 1mol/lit, 1.5 mol/lit, 2 mol/lit, 2.5 mol/lit.
- For catalyst loading variation, experiment was carried out at 0.00 gm, 0.125gm or 0.01228, 0.25 gm or 0.02456 mol/lit, 0.45 gm or .0442 mol/lit & 0.75 gm or 0.0737 mol/lit.
- The 9 samples of organic phase for each reaction was analysed in GC.

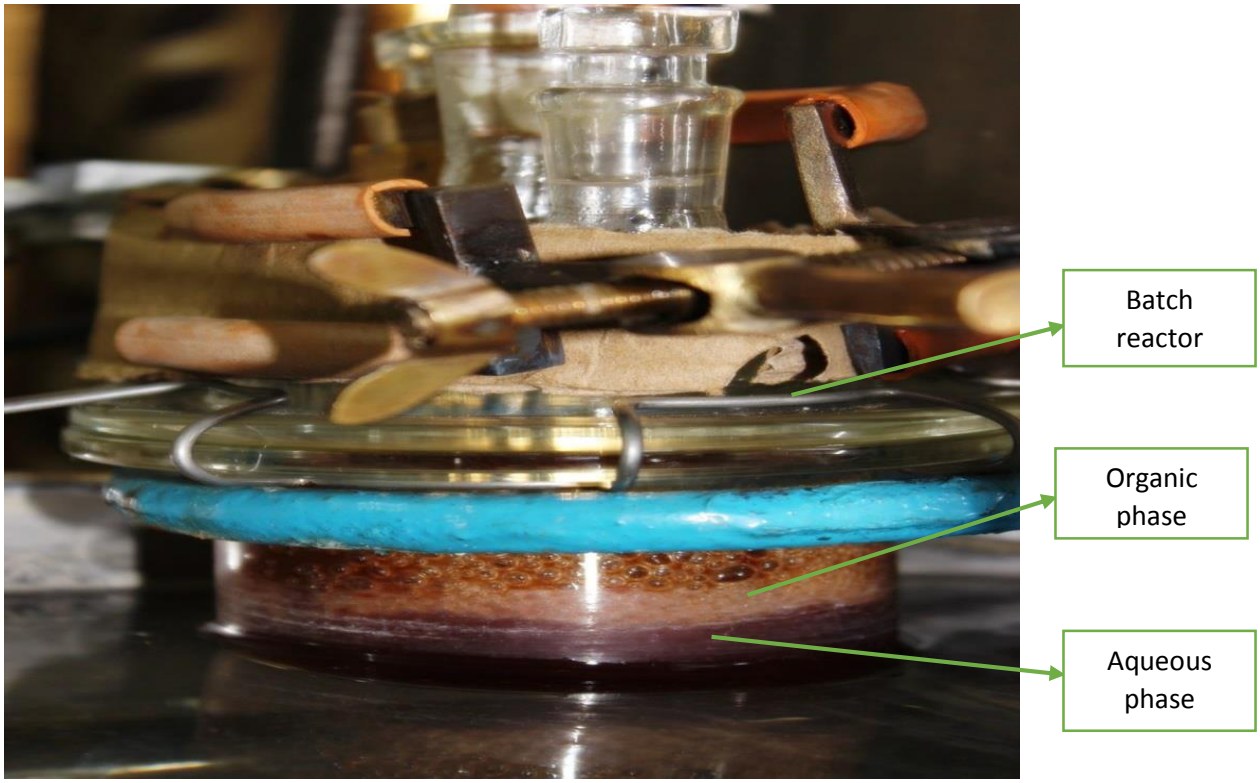


Fig 3.4 Showing Organic & aqueous phase in a batch reactor

3.6 ANALYSIS OF ORGANIC PHASE

Gas chromatography is a common type of chromatography used for quantitative analysis of vaporized compound without decomposition. It tests the purity of a particular substance by separating a mixture of different components.

In GC mobile phase is a carrier gas, normally consist of unreactive or inert gas like He, Ar, N etc. The stationary phase is microscopic layer of high boiling polymer coat & solid support in a packed column. Most of the analytical GC use capillary columns which is coated on the inner side of the wall with high boiling polymer.

The flame ionisation detector vaporize the organic phase & carrier gas carries vaporized organic compound inside the capillary or packed column. Then the gaseous compound interact with the liq. Coating of polymer or stationary phase. The separation of compounds is entirely based on interaction with stationary phase. The stronger the interaction more the time required to elute through stationary phase. Hence different retention time. Thus we get 3 different peaks at different times for toluene, reactant & product.

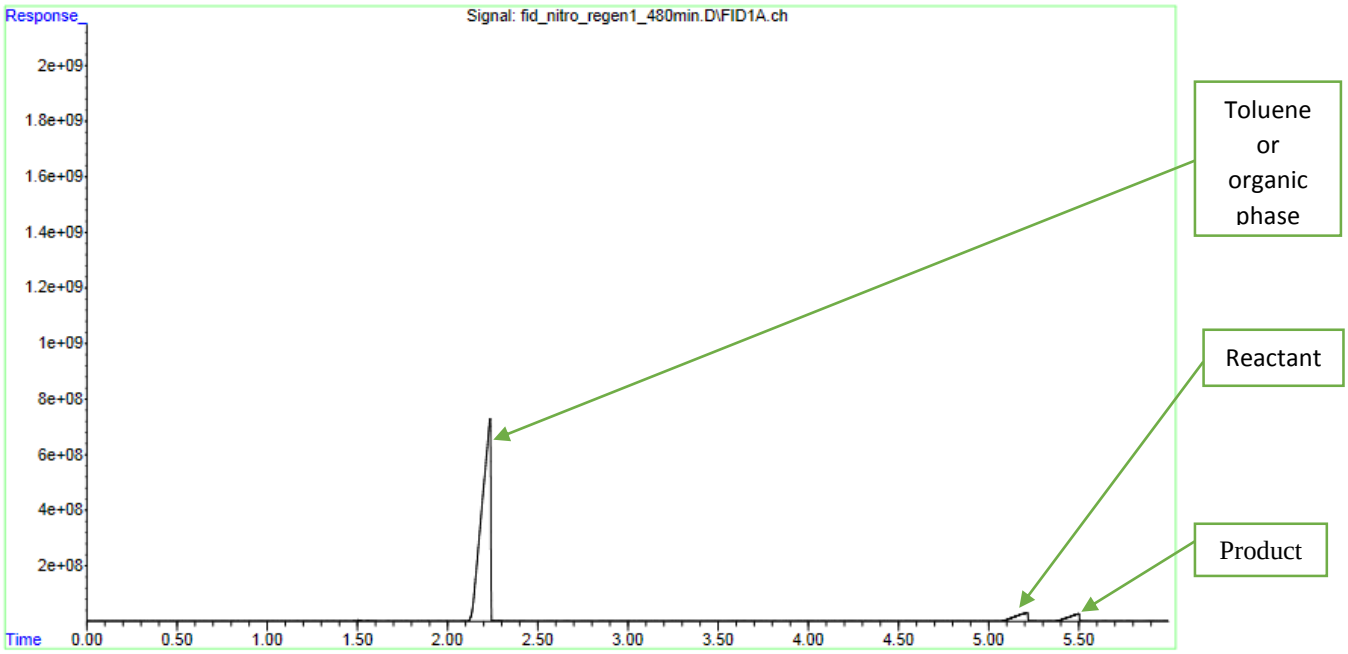


Fig 3.5.1 Response vs Retention time at 480 min

Fig 3.5.2 Gas Chromatograph

REF: http://www.se-source.com/gc.htm

CHAPTER-4

4 Results & Discussion

4.1 Abstract

The entire work focus on the reaction of 3-NAP with MDEA in presence of phase transfer catalyst tetrabutylphosphonium bromide to produce 3-AAP. The effect of various parameters on the synthesis of 3-AAP. The parameters studied in detail in the current project are

- ✓ Effect of temperature
- ✓ Effect of stirring speed
- ✓ Effect of reactant concentration
- ✓ Effect of sulphide concentration
- ✓ Effect of catalyst loading

4.2 RESULTS

4.2.1 EFFECT OF TEMPERATURE

The rate of reaction is greatly influenced by temperature since the energy of activation & rate of conversion depends upon the system temperature. Keeping other operating condition constant the effect of temperature on conversion of 3-NAP was studied in the range of 313K-343K. A graph was plotted between conversions of 3-NAP vs time for various temperatures. According to collision & transition state theory reaction occurs only when particles with certain minimum energy collide. Increasing the temperature causes gain in energy of particles. Hence they move faster & collide more frequently which will speed up the reaction. From the experiment it was found out that reaction rate approximately doubles for each 10^0C rise in temperature.

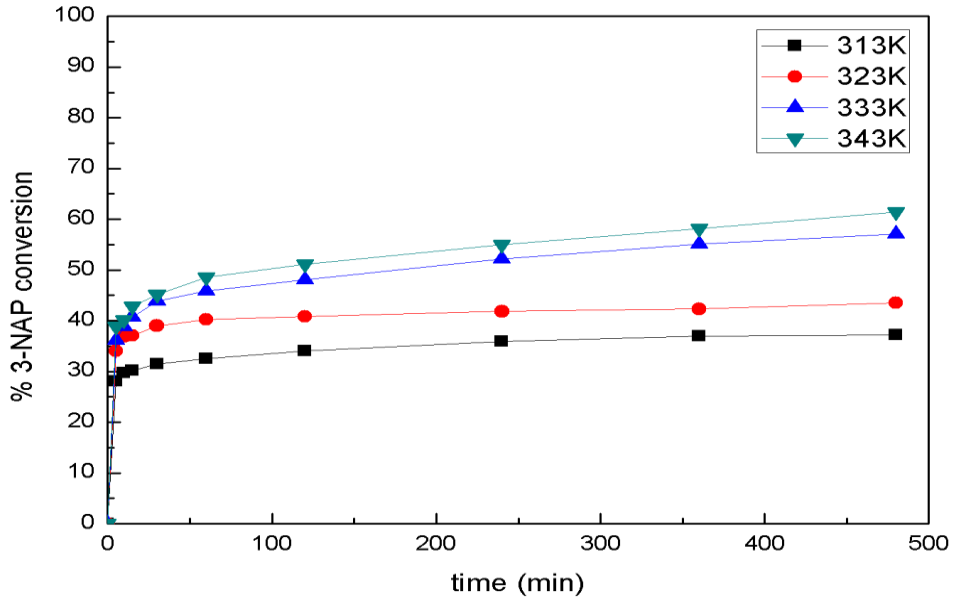


Fig 4.1.1 Effect of temperature on conversion of 3-NAP

Operating conditions: Organic phase volume =30 mL; Aqueous phase volume = 50 mL; sulphide concentration = 2.5 mol/lit; MDEA concentration = 3.04 mol/lit; catalyst concentration = 0.0442 mol/lit; reactant concentration = 0.9082 mol/lit; stirring speed=1500 rpm.

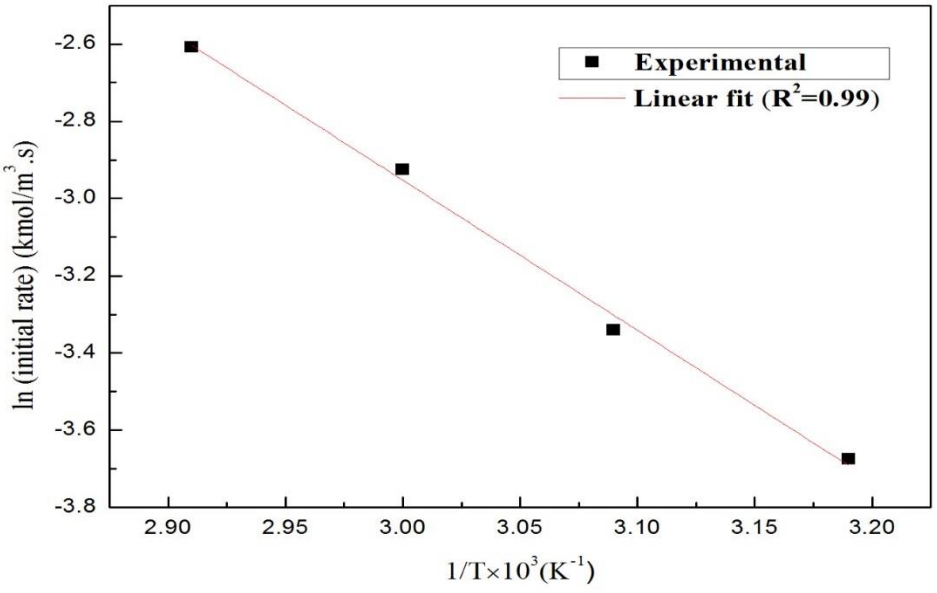


Fig 4.1.2 Arrhenius plot

$$\therefore According\ to\ Arhenius\ theory$$

$$ln\ \frac{K_1}{K_2} = ln\ \frac{r_1}{r_2} = -\frac{E}{R} * \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

A plot of ln (initial rate) vs 1/T x 10^{-3} (K^{-1}) is drawn & the apparent energy of activation for conversion of 3-NAP was found from the slope of the straight line to be 9.386KJ mol^{-1}. It ascertains the fact that reaction is kinetically controlled.

$$slope = -\frac{E}{R} = -1.129$$

$$\Rightarrow E = -1.129 * 8.314 = 9.386\ KJ\ mol^{-1}$$

4.2.2 EFFECT OF STIRRING SPEED

Since this reaction is a two phase reaction mass transfer plays very crucial role. Resistance to mass transfer builds up if the solution is not stirred. Keeping the other conditions identical stirring speed is varied from 500 rpm to 2500 rpm. A plot of % 3-NAP conversion vs time is plotted & analysed for various stirring speed. Then average reaction rate corresponding to each stirring speed is determined & plotted against stirring speed. From the plot it was assumed that around 500-1000 rpm the reaction rate increases slightly with increase in stirring speed. But after 1500 rpm the reaction rate is approximately same because the mass transfer resistance disappear around 1500 rpm & contributes very trifling amount to conversion of 3-NAP.

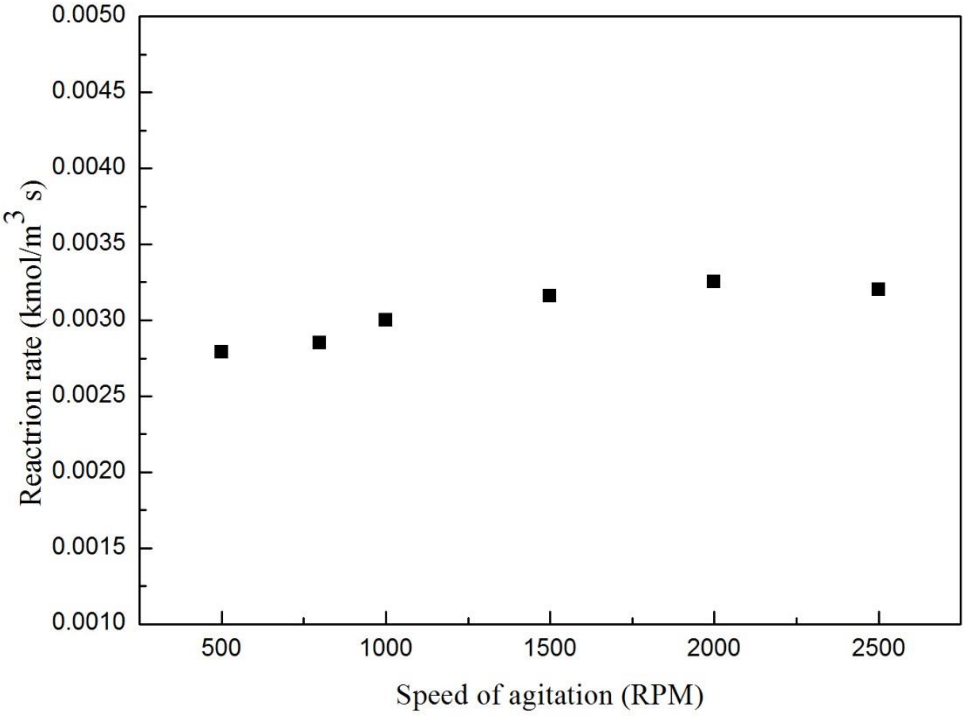


Fig 4.2 Effect of stirring speed on the conversion of 3-NAP

Operating condition: Organic phase volume =30 mL; Aqueous phase volume = 50 mL; sulphide concentration = 2.5 mol/lit; MDEA concentration = 3.04 mol/lit; catalyst concentration = 0.0442 mol/lit; reactant concentration = 0.9082 mol/lit; temperature = 50^0C or 223K.

4.2.3 EFFECT OF REACTANT CONCENTRATION

The effect of 3-NAP concentration on the conversion 3-NAP itself was studied at four different 3-NAP concentration at 1.5 gm or 0.3027 mol/lit, 3gm or 0.6055 mol/lit, 4.5gm or 0.9082 mol/lit, 6gm or 1.21 mol/lit. A plot of % 3-NAP conversion vs time for four different initial concentration is drawn. From the plot it was figured out that with increase in 3-NAP concentration the conversion of 3-NAP decreases because of limited quantity of sulphide present in the aqueous +phase. As HS^- present in aqueous phase plays important role in first step of reaction. So with limited sulphide concentration increase in 3-NAP lead to fall of % 3-NAP conversion.

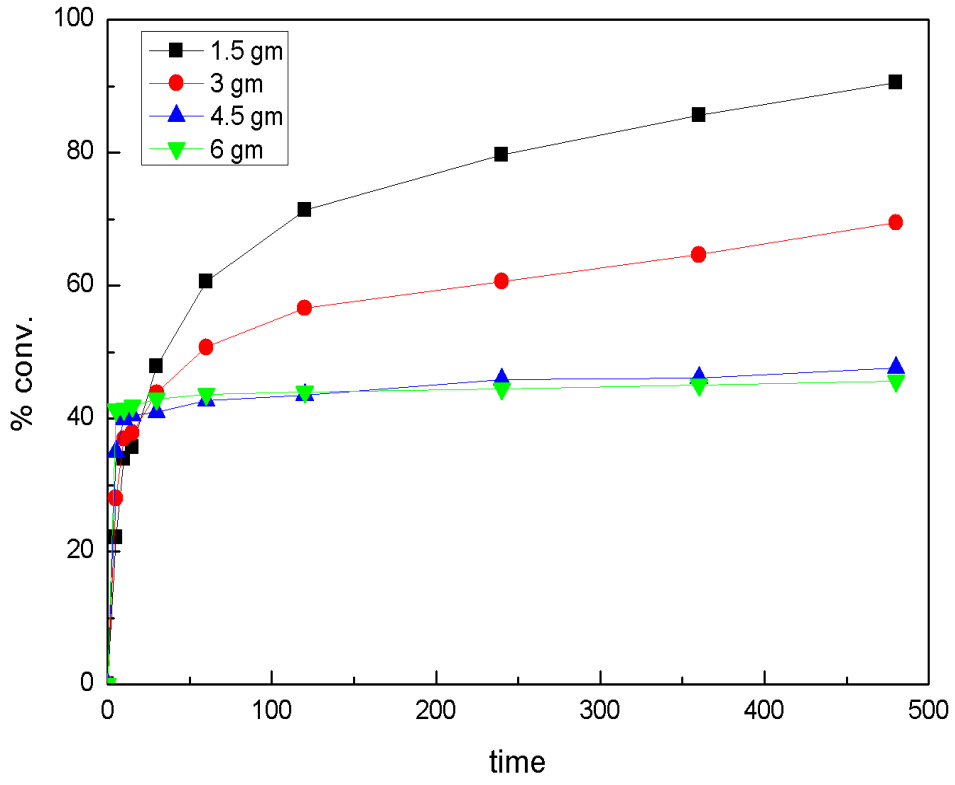


Fig 4.3.1 Effect of initial reactant concentration on conversion of 3-NAP

Operating condition: Organic phase volume =30 mL; Aqueous phase volume = 50 mL; sulphide concentration = 2.5 mol/lit; MDEA concentration = 3.04 mol/lit; catalyst concentration = 0.0442 mol/lit; stirring speed = 1500 rpm; temperature = 50^0C or 223K.

The order of the reaction is found to be 0.45≅0.5 from the order plot.

So

$$r = K\,[reactant\ concentration]^{0.5}$$

The natural logarithm of reactant concentrations were plotted against natural logarithm of initial reaction rates as shown in the figure . A linear fit is obtained for all the points in the graph. The slope of the line was found to be 0.454.

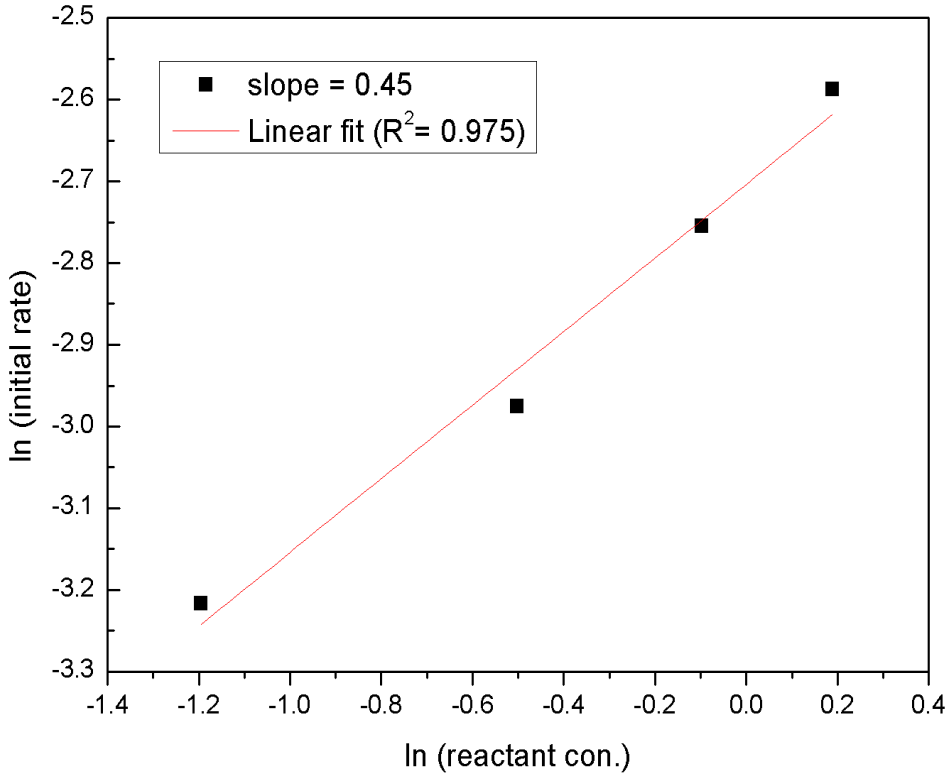


Fig 4.3.2 ln (initial rate) vs ln (reactant concentration)

4.2.4 EFFECT OF CATALYST LOADING

The effect of concentration of catalyst TBPB was studied in the present work. The catalyst plays crucial part in the conversion of 3-NAP to 3-AAP. Catalyst normally lowers the activation energy for the reaction without reacting itself or being inert throughout the reaction. The effect of catalyst on conversion of 3-NAP was studied for the catalyst loading of 0.00 gm, 0.125gm or 0.01228, 0.25 gm or 0.02456 mol/lit, 0.45 gm or .0442 mol/lit & 0.75 gm or 0.0737 mol/lit. The graph is plotted against % 3-NAP conversion vs time for various catalyst loading. From the graph it was found that the rate of conversion of 3-NAP to 3-AAP increases with increase in catalyst loading.

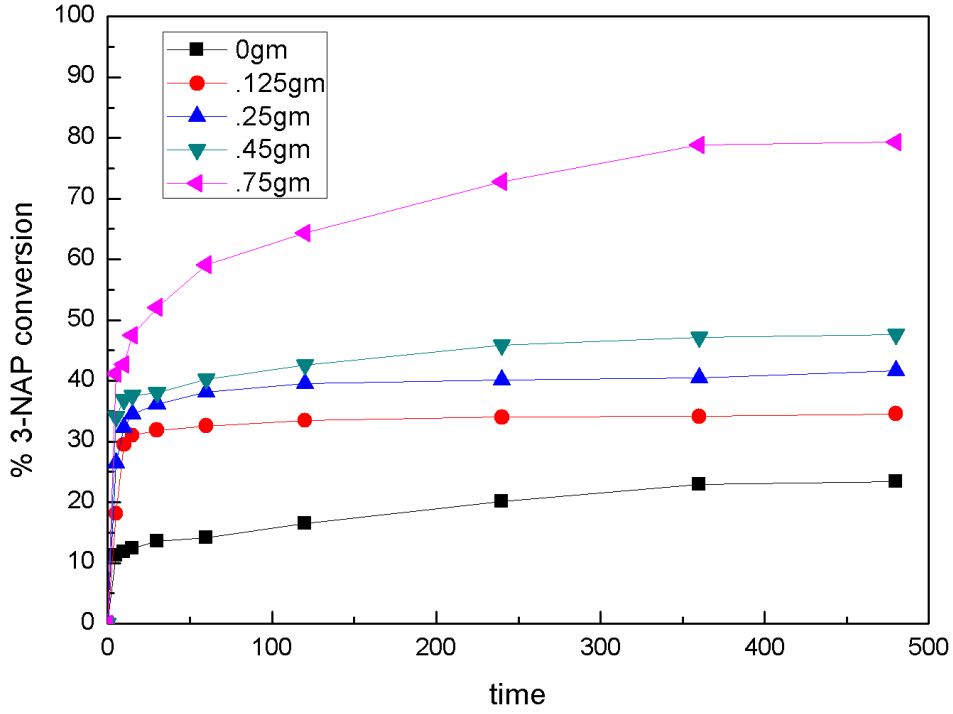


Fig 4.4.1 Effect of catalyst concentration on conversion of 3-NAP

Operating condition: Organic phase volume =30 mL; Aqueous phase volume = 50 mL; sulphide concentration = 2.5 mol/lit; MDEA concentration = 3.04 mol/lit; reactant concentration = 0.9082 mol/lit; stirring speed = 1500 rpm; temperature = 50^0C or 223K.

The order of the reaction is found to be 0.45≅0.5 from the order plot.

So

$$r = K\,[catalyst\ concentration]^{0.5}$$

The natural logarithm of initial reaction rates were plotted against natural logarithm of TBPB concentration as shown in Fig 4.1.1. Linear fit was applied to all the points in the graph. The slope of the line was found to be 0.45.

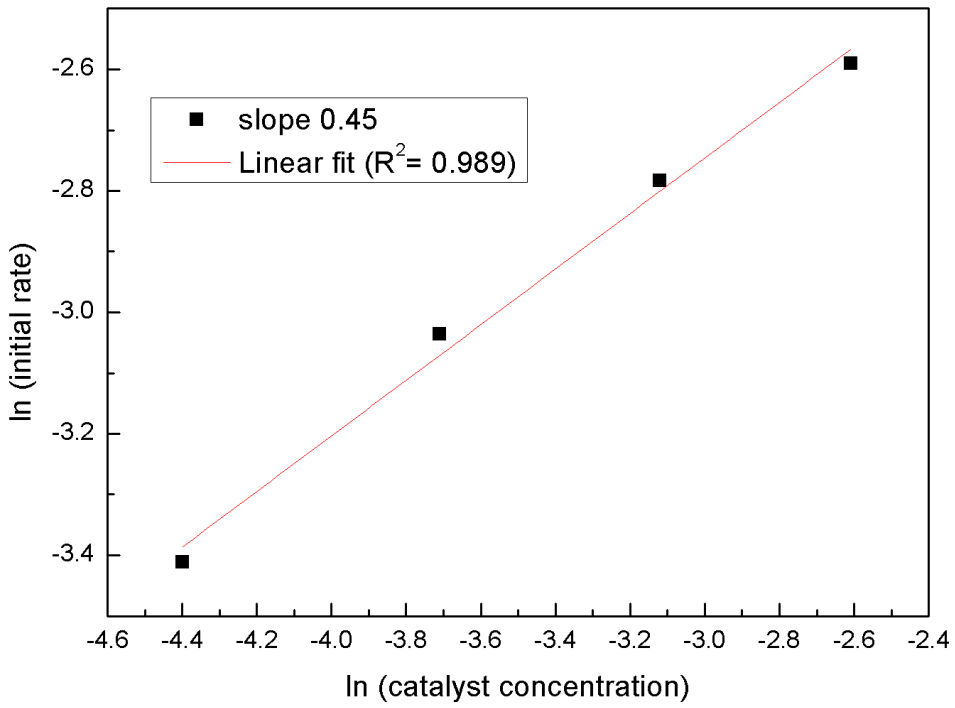


Fig 4.4.2 ln (initial rate) vs ln (catalyst concentration)

CHAPTER-5

5 Conclusion

A commercial interest novel substitute to Claus process, reduction of 3-nitroacetophenon to 3-aminoacetophenon by H_2S rich aqueous n-methyldiethanolamine under the catalytic effect of phase transfer catalyst tetrabutylphosphonium bromide was studied. The reduction was studied for various different combination of process parametric variables. Effect of variation of temperature, effect of variation of stirring speed, effect of variation of catalyst loading & effect of variation of reactant concentration.

The product obtained in this work is 3-AAP which is an excellent intermediate for preparing pharmaceutical drugs like pectamycin, synthesis of new effective catalysts for various process, manufacturing of pesticide, manufacturing of HPCL silica monolith, preparation of unnatural amino alcohol containing an aging flavour called UTA, bee repellents, Immobilization of E. Coli & much more uses with small scale commercial importance like Spectrophotometric determination of isoproturon etc.

From the study of effect of variation of temperature it was found out that for each 10^0C rise in temperature the reaction rate doubles. According to collision & transition state theory reaction occurs only when particles with certain minimum energy collide. Increasing the temperature causes gain in energy of particles. Hence they move faster & collide more frequently which will speed up the reaction. The activation energy was found out to be 9.386 KJ mol^{-1} from Arrhenius plot.

From the study of effect of variation of stirring speed it was found out that low stirring speed around 500 rpm -1000 rpm the mass transfer resistance plays crucial role in affecting the rate of reaction. But around 1500 rpm or above the mass transfer resistance disappears & its effect on rate of reaction is frippery. Hence the reaction rate increases while varying the stirring speed ranging from 500 – 1000 rpm & remains almost constant above 1500 rpm. Hence 1500 rpm being optimum agitation speed, it was used as constant value for other variation.

From the study of effect of variation of reactant concentration it was found out that the rate of reaction decreases with increase in reactant concentration keeping the initial sulphide concentration same. Normally the rate of reaction increases on increasing the concentration of reactant because the no of particles in the same volume increases. Hence the chance of no. of

collisions increases leading to increase in reaction rate. But there are certain exception like where catalyst is present & working as fast as it can and certain multistep reactions. This is a multiple step reaction, concerning first step is the transfer of HS^- by phase transfer catalyst TBPB from aqueous phase to organic phase. Hence the rate of reaction depends upon the amount of HS^- available for reacting with reactant. That is also the exact reason why rate of reaction depends upon sulphide concentration. So keeping the sulphide concentration & increasing the reactant concentration decreases the rate of reaction.

From the study of effect of variation of catalyst concentration it was found out that increase in catalyst concentration increases the rate of reaction. There are two ways of increasing the rate of reaction one possible way is increasing the no. of successful collisions & other alternate is lowering the activation energy required to make the reaction happen. Catalyst does not lower the activation energy rather provides an alternate route for the reaction with a lower activation energy & speeds up the reaction being chemically unreacted at the end of reaction.

CHAPTER-6

6 Future work

This content reflects on the further continuation of the present work to cultivate an industrial model, a substitute to Claus process, of commercial importance.

6.1 Effect of other parameters

The present work involves study of effect of temperature, effect of stirring speed, effect of reactant concentration & effect of catalyst loading. Here only one parametric variable is varying remaining constant. But there are other parametric variations that can be done like varying two or three parametric variation at a time

- Effect of different catalysts like TBAB, Amberlite 400 on conversion of 3-NAP to 3-AAP.
- Effect of sulphide concentration keeping reactant concentration constant.
- Effect of sulphide concentration with varying reactant concentration.
- Effect of temperature with varying catalyst concentration
- Effect of catalyst concentration with varying temperature

There are overall six parametric variables. By trying out different other combinations of parametric variations the exact dependency of rate of reaction for conversion of 3-NAP to 3-AAP can be found out. Linking to that result a complete kinetic model for conversion of 3-NAP can be predicted based on phase transfer catalysis.

6.2 Effect of solvents

In the present work keeping the fact that H_2S is primary agent for removal or utilization, MDEA had been chosen. Since MDEA is H_2S selective, for a gas stream containing both H_2S & CO_2 using MDEA is not advisable. There comes MEA which can absorb both H_2S & CO_2. Likewise the present work can be carried out for different other solvents like Sulfinol M/D, Ucarsol, Flexsorb etc. These solvents are normally used for enrichment of acid gas.

6.3 Effect of Organic phase

In the present work toluene is used as organic phase. For PTC systems almost any organic solvents can be used. Some industrial phase transfer catalysis have even adopted solvent-free PTC conditions when reactant is liquid & can be used in excess. This present work can be carried out for other organic solvents like DMSO, DMF, NMP, DMA etc.

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